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To (Name) Mr. J. A. Parsons	Date January 21, 1960
Company	
Location K-303-8	Originating Dept. Production Engineering
	Answering letter date
Copy to Mr. A. L. Allen	Subject Distribution and Recovery
Mr. H. A. Bernhardt	of Technetium at ORGDP
Mr. E. C. Bollinger	
Mr. J. Dykstra	
Mr. A. P. Huber	
Mr. M. F. Schwenn	
Mr. R. D. Shaffer	
Mr. A. Varlan	
File	

Prod. Div. File

Classification changed to 20 Unclassified
(level and category)

By authority of: CG-PGD-4
(classification guide)

9/21/94
ADC or ADD signature (first reviewer)   Date

22 Sep 94
ADD signature (final reviewer)   Date

In view of the recent interest in many of the trace elements, preliminary studies have been conducted to determine the concentration of technetium in various feed plant streams and also to determine a suitable method for technetium recovery.   The results of the study are summarized, including recommendations and associated costs for a recovery system.

SUMMARY

1. In the feed plant system, technetium tends to concentrate in fluorination system ash, ranging from 1 gram per ton of uranium in the fluorination tower ash to 42 grams per ton of uranium in the barrier filter ash.

2. Soak tank solution ($\sim$20% ammonium carbonate) resulting from the cleaning of feed plant equipment was found to contain up to 6 ppm technetium.

3. Based on the current inventory and accumulation rate of soak tank solution and the accumulation rate of barrier filter ash from Savannah River oxide processing, approximately 260 grams of technetium could be recovered from these two streams during the next year.

4. A preliminary design for technetium recovery is shown in a flow diagram which is incorporated with the proposed uranium recovery process for feed plant scrap at K-1410.

The estimated cost to recover technetium as impure ammonium pertechnetate using pyridine as the extractant as shown in the flow diagram is $63.70 per gram.   This is based upon a $525 cost to process each batch recovering .

This document has been approved for release to the public by:

A. S. Iouis   6/11/96
Technical Information Officer   Date
Oak Ridge K-25 Site
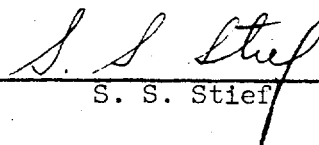
8.5 grams of a contained 15 grams per batch. The rather low recovery efficiency of 55 percent is based upon the relatively high solubility of pyridine in 2 molar concentration of ammonium carbonate solution as experienced in laboratory work.

5. Although the flow diagram shows a pyridine-aqueous system, the pyridine can be replaced with alpha picoline with comparatively little change in process equipment. Alpha picoline is cheaper than pyridine, has a much higher technetium distribution coefficient than pyridine, and is much less soluble in the aqueous. From these data, as reported by ORNL, it is recommended that alpha picoline be used.

6. The estimated cost to recover technetium as impure ammonium pertechnetate using alpha picoline as the extractant in essentially the same process as shown is $35.40. This is based upon a $478 cost to process each batch recovering 13.5 grams of a contained 15 grams per batch. The 90% recovery efficiency is based upon ORNL data reporting 2 or 3 ml. alpha picoline soluble per 100 ml. of 2 molar ammonium carbonate.

7. The estimated capital investment required for the pyridine-aqueous process as shown in the flow diagram is $38,378. For alpha picoline, the capital investment is anticipated to be approximately $35,000 because of the decreased solubility resulting in less recovery steps for the organic.

The following attachments present more detailed information concerning technetium recovery operations and a schematic sketch of a proposed recovery system.

S. S. Stief

SSS:jc

FEED PLANT SURVEY

In order to establish analytical data concerning the distribution of technetium in the feed plant streams, a controlled sampling program was initiated during the processing of approximately 300 tons of Savannah River reactor tails oxide. A brief summary of the sampling program procedure follows:

1. The feed plant system was "flushed-out" with approximately 150 tons of Savannah River material before sampling was started.

2. A new barrier filter was installed in one fluorination tower outlet gas header and ash receivers were changed on the primary tower, cyclone and barrier filter.

3. At the end of the survey, the above units were changed again so that they were exposed only to Savannah River material.

4. One sintered metal tube from the clean-up reactor filter was also installed before the test and removed at the end for sampling purposes.

5. In most cases, duplicate samples of all outgoing streams from the process were taken. Samples were also taken of the intermediate products such as UO_2, UF_4 and gas phase UF_6.

6. Off-gas samples were collected by passing a side stream of the off-gas through a saturated solution of ammonium carbonate. The efficiency of this method for collecting the technetium as the ammonium pertechnetate compound has not been established.

7. At the conclusion of the test, barrier filter tubes were cleaned with ammonium carbonate solution and the solution analyzed for technetium.

8. All samples were sent to ORNL for technetium analyses.

A summary of the analytical results is presented in table 1. Results are expressed in micrograms of technetium per gram or milliliter of sample, and, where possible, in grams of technetium per ton of contained uranium in the sample. Figure 1 presents a simple flow diagram of the feed plant process showing the points at which the samples were taken. In analyzing the data of the feed plant survey, several comments can be made:

1. There is no appreciable loss of technetium in the reduction of UO_3 to UO_2. The concentration of technetium in the Savannah River oxide feed is 4.835 grams per ton of uranium while the product UO_2 contains 4.735 grams per ton of uranium.

2. Although the analytical data indicate that there is an appreciable loss of technetium in the hydrofluorination step, there is evidence that the analytical procedures used for technetium determination in samples containing fluoride ions probably produce results which are biased low. Small concentrations, however, were detected in the recovered hydrous HF stream and also in the hydrofluorination system vent gas.

3. There are indications that volatile fluorides of technetium are formed in the fluorination system. Technetium is not only found in the UF_6 gas stream but also in various concentrations in the ash collectors after the tower and clean-up reactor. For example, the technetium

concentration in the tower ash collector (highest gas temperature) is 1.68 micrograms compared to 68 ± 5 micrograms in the barrier filter ash collector (lowest gas temperature).

4. Appreciable quantities of technetium were found in the product UF_6, however, the results of four separate samples showed a wide variation of concentration.

5. From the data of the survey, it was not possible to calculate a reliable material balance. However, it is apparent that technetium tends to concentrate in the fluorination ash, and more specifically, in the ash collected at the barrier filters. This material, therefore, represents the richest source for technetium recovery in feed plant streams.

ANALYTICAL RESULTS OF TECHNETIUM SURVEY
AT K-1131

Sample No.	Origin	Technetium Analyses μ g/g of sample	g/ton of U
1	UO_3 (composite of Lots 884, 885, 886)	6.4	4.835
2	UO_2 from fluid bed	5.92	4.735
3	H_2 system off-gas in $(NH_4)_2 CO_3$ solution	0	0
4	H_2O - after cooler-reduction system	*<0.4, <0.1	-
5	UO_2 from No. 2 conveyor	6.0	4.796
6	UF_4 - Product hopper	2.35	1.617
7	HF system off-gas in $(NH_4)_2 CO_3$ solution	*<0.1	-
8	Hydrous HF	*<0.1	-
9	UF_4 from No. 2 conveyor	2.76	1.899
10	UF_6 gas sample (after No. 1 tower)	* 0.42	3.222
11-A	Hydrolyzed UF_6 - Modine trap	* 0.13	5.901
11-B	Hydrolyzed UF_6 - CO_2 trap	* 1.6	72.64
11-C	Hydrolyzed UF_6 - Modine trap	* 0.27	12.25
11-D	Hydrolyzed UF_6 - CO_2 trap	* 0.14	6.356
12	F_2 system off-gas in $(NH_4)_2 CO_3$ solution	*<0.02	-
14	UO_2 from reduction system filter	5.45	4.359
15	UF_4 from HF system filter	8.03	5.528
16	Ash from tower receiver	1.68	1.037
17	Ash from tower cyclone receiver	8.1	5.00
18	Ash from tower barrier filter receiver	73.6, 63	Avg.41.983
18-A	Cleaning solution from barrier filter tubes	* 0.042	-
19	Ash from tubes of barrier filter	5.94	3.666
20-A	Cleaning solution from C.U. reactor barrier filter tubes	* 0.83	-
21	Ash from sintered tube - C.U. reactor	14.8	9.139
21-A	Cleaning solution from sintered tube - C. U. reactor	* 0.82	-
21-B	Powder from C.U. reactor filter	21.45	13.241

* Tc results expressed in μ g/ml of solution.

INVENTORY OF RECOVERABLE TECHNETIUM

Prior to the feed plant survey for technetium, it was found that the cleaning solution ($\sim$20% ammonium carbonate) which is used for the cleaning of feed plant equipment at K-1410 also contained recoverable quantities of technetium. It is estimated that approximately 125 grams of technetium are available for recovery in the current inventory of cleaning solution. Based on present operations at K-1410, the annual accumulation of technetium in this solution is estimated at 65 grams.

The annual accumulation of barrier filter ash from the ORGDP feed plant is approximately 2,300 pounds containing 71 grams of technetium. Although efforts are continuing in an attempt to identify technetium distributions in other ORGDP process or waste streams, the K-1410 cleaning solutions and barrier filter ash appear to be more suitable for a recovery operation.

In this regard, a suitable method for technetium recovery from alkaline solutions has been investigated on a laboratory-scale at ORNL. In general, technetium is extracted from an aqueous alkaline solution by pyridine; the pyridine is distilled off, leaving the technetium in the still residue as ammonium pertechnetate. A more complete discussion of a proposed recovery system and associated costs are presented in the following section.

DISCUSSION OF RECOVERY PROCESS

From laboratory data gathered for a pyridine-aqueous system, a preliminary recovery process for technetium as ammonium pertechnetate was designed. The design is shown as a flow sheet in figure 2. The process would be located in K-1410 building and be linked to the uranium recovery unit.

The process in general consists of the following steps:

1. The soak tank solution is evaporated from 1000 to 500 gallons when the uranium concentration reaches approximately 10 percent by weight. The technetium concentration at this point is assumed to be 4 ppm, or a total of 15 grams per 500 gallons.

2. The concentrated aqueous is centrifuged to remove insolubles. These are calcined and drummed for later uranium recovery.

3. The effluent from the centrifuge flows to a holding tank, equipped with an agitator, where 214 pounds of ammonium carbonate is added to make the solution 2 molar in order to reduce the solubility of pyridine in the aqueous.

4. The aqueous (which has now increased in volume) is pumped to a continuous mixer agitated column where it is contacted with pyridine in the ratio of 100 volumes of aqueous to 37 volumes of 76% pyridine. The upper portion of the column is not agitated to allow the lighter organic to separate and flow to a storage tank. The heavier aqueous, containing the uranium, flows from the bottom of the column to a holding tank. The aqueous also contains dissolved pyridine in the ratio of approximately 1 gallon of pyridine to 7.2 gallons of aqueous and, for this reason, must be heated to recover the pyridine.

5. The pyridine, from the mixer-settler column, flows to a small holding tank as an azeotrope composed of 57 percent by weight of pyridine and 43 percent of water. (An azeotrope is a mixture that is constant boiling and has constant composition at constant pressure.) The anticipated volume of azeotrope is 141 gallons and contains the product ammonium pertechnetate.

6. The pyridine azeotrope is pumped to a batch still where some excess water is added. Ammonium carbonate is driven off first at 80°C. and must be vented. The azeotrope boils at 92.6°C. and is condensed and collected in a holding tank. When the boiler temperature rises to 105°C., all the pyridine has been removed and the ammonium pertechnetate remains in solution as the still residue. This residue is tapped off the still boiler to a drum. The impure ammonium pertechnetate concentrate is considered the ORGDP product and is shipped to ORNL for further refinement as the pertechnetate, oxide or metal.

7. The aqueous from the mixer-settler containing pyridine is then pumped to the batch still and the pyridine boiled off and collected as azeotrope. When the temperature rise is noted in the still boiler, the aqueous residue is valved from the boiler to the uranium recovery unit. A total of approximately 248 gallons of azeotrope are collected in the still receiver tank from steps 6 and 7.

8. The pyridine azeotrope distillate must be at least partially dehydrated before it can be reused as an extracting agent. A 4 M sodium carbonate, 0.5 M sodium hydroxide solution added to the azeotrope and agitated for several minutes removes 57 gallons of water and converts the azeotrope to a 75-25 percent pyridine-water mixture.

9. The pyridine-sodium carbonate aqueous mixture is pumped to a settler column and the aqueous layer is discarded. The upper organic layer of approximately 191 gallons of 75-25 percent pyridine-water is pumped back to the organic storage tank where 5 gallons of 100% pyridine are added as make-up. The cycle is completed at this stage.

The process is primarily a batch type with only the mixer-agitated column operating continuously until the feed tanks are pumped dry. Barrier filter ash would be introduced into the system at the soak tank. Batch quantities would be dissolved in a solution of ammonium carbonate and hydrogen peroxide and pumped to the centrifuge as soak tank solution.

The process was designed using pyridine as the organic because of original research work performed at ORNL. More complete data were obtained in the Process Laboratory. In the meanwhile, alpha picoline was discovered at ORNL to be a better extractant of technetium. Alpha picoline is far less soluble (12 times less), in 2 M ammonium carbonate solution than pyridine. Also, the distribution coefficient of technetium in the organic is 243 using alpha picoline as compared to 7.57 using pyridine. An azeotrope is also formed with alpha picoline and water. Since alpha picoline costs $0.26 per pound less than pyridine and is less soluble in aqueous, the cost to recover technetium would be less by using the former organic. A more important point would be that a much higher recovery efficiency would be attained because of the greater distribution coefficient and, therefore, a further cost reduction would be realized.

Although alpha picoline appears to have definite advantages over pyridine, cost calculations were based on a pyridine system because no actual laboratory data have been obtained in the Process Laboratory using alpha picoline. This organic has been ordered so that laboratory investigations can proceed. From the above data, however, it appears likely that alpha picoline will replace pyridine without many changes in the processing system. Therefore, it is estimated that, under the same conditions, technetium would be recovered for $35.40 per gram using alpha picoline and $63.70 per gram using pyridine. Current recovery costs at ORNL are approximately $2800 per gram.

Capital costs for the design and installation of the pyridine extraction system have been estimated at $39,000.

ESTIMATED COST TO RECOVER TECHNETIUM - PYRIDINE SYSTEM

Basis: 500 gallon batch containing 15 grams total (4 ppm) of technetium.

	Cost/Batch
Labor (1 operator for 20 hrs. at $2.94/hr.)	$ 58.90
Maintenance Labor (10% of direct labor)	5.89
Supervision (4.5 hrs. at $36.60/day)	20.20
Total Labor	$ 84.99
Overhead (116% of all Labor)	98.19
Maintenance Material (5% of direct labor)	2.95
Raw Materials:	
Ammonium carbonate	214.00
Sodium carbonate	12.20
Sodium hydroxide	1.23
Pyridine	68.00
Total Raw Materials	$295.43
Utilities (steam, electricity)	8.10
Other Material (lab. analyses, 2 req.)	35.00
Total	$524.66
Say	$525/batch

Percent recovery estimated, 55%

Cost per gram impure Tc recovered $= \dfrac{525}{(15)(.55)} = \$63.70$
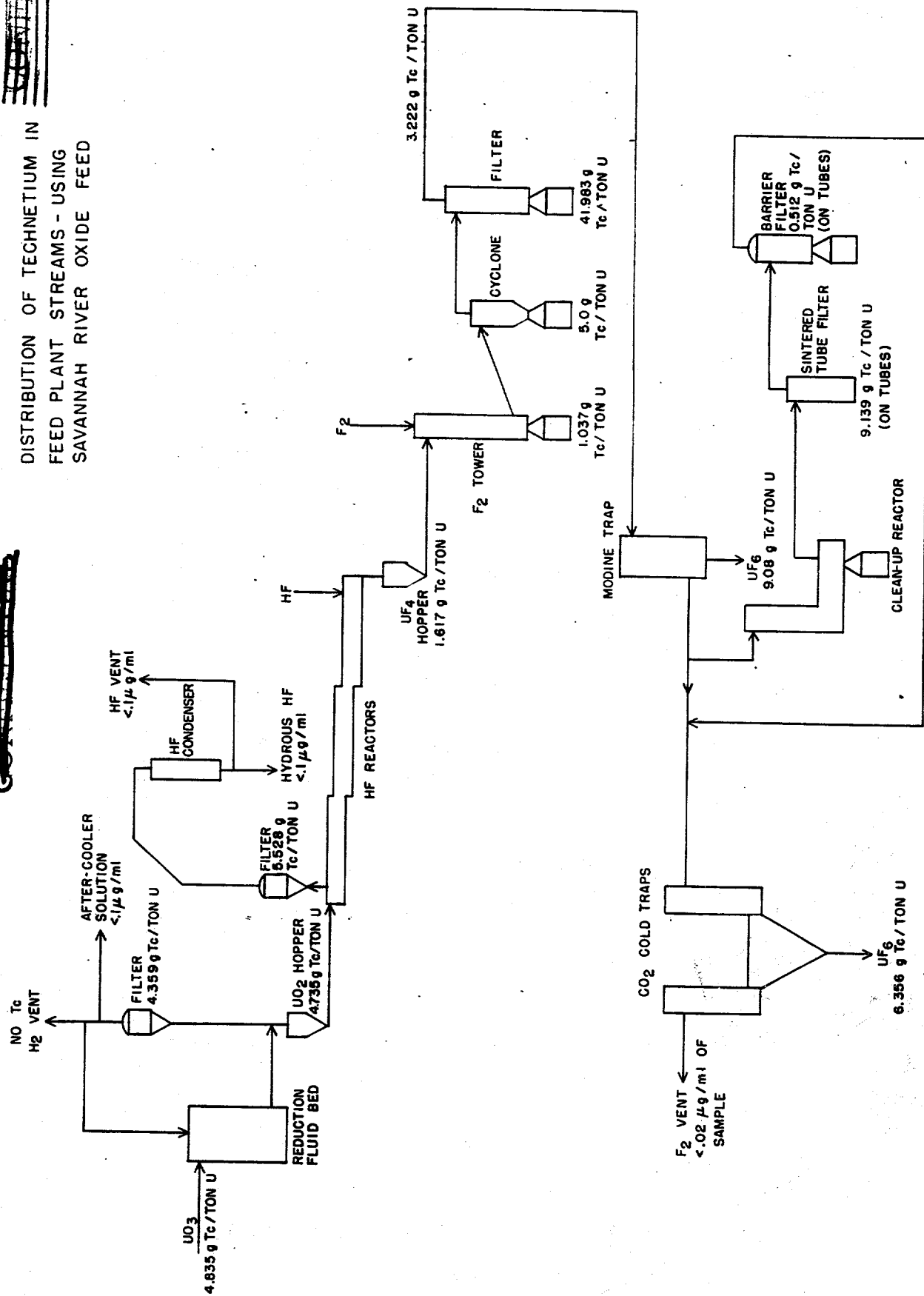
ESTIMATED CAPITAL INVESTMENT

Item	Cost, 1955
6 Steel Tanks, 2 agitated, 1 jacketed	$ 9,200
6 Pumps	1,550
2 Motors, open	300
4 Motors, explosion proof	1,000
4 Flame Arrestors	800
1 Condenser	200
1 Mixer Column, 15 ft. agitated	2,000
1 Settler Column, 15 ft.	400
2 Flowrators	300
3 Liquid Level Indicators	480
Purchased Equipment Cost	$16,230

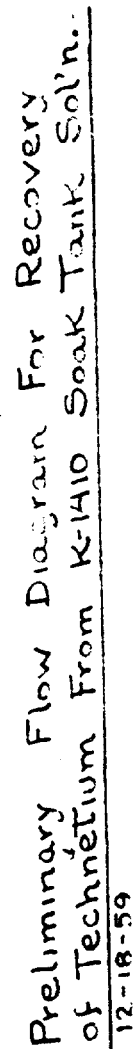|	
Purchased Equipment Cost, 1960 (10% increase)	$17,853
Equipment Installation (43% of Purchased Equipment Cost)	7,670
Piping (25% of Purchased Equipment Cost)	4,460
Other Instrumentation (3% of Purchased Equipment Cost)	540
Electrical Work (15% of Purchased Equipment Cost)	2,680
Insulation (4% of Purchased Equipment Cost)	710
Engineering (10% of Purchased Equipment Cost)	1,785
Contingencies (15% of Purchased Equipment Cost)	2,680
Total Capital Investment Cost	$38,378

DISTRIBUTION OF TECHNETIUM IN
FEED PLANT STREAMS - USING
SAVANNAH RIVER OXIDE FEED

UO_3
4.835 g Tc/TON U

REDUCTION FLUID BED

NO Tc H_2 VENT

FILTER
4.359 g Tc/TON U

AFTER-COOLER SOLUTION
$<.1\mu g/ml$

HF CONDENSER

HF VENT
$<.1\mu g/ml$

HYDROUS HF
$<.1\mu g/ml$

FILTER
6.528 g Tc/TON U

UO_2 HOPPER
4735g Tc/TON U

HF REACTORS

HF

UF_4 HOPPER
1.617 g Tc/TON U

F_2

F_2 TOWER

1.037g Tc/TON U

CYCLONE

5.0 g Tc/TON U

FILTER

3.222 g Tc/TON U

41.983 g Tc/TON U

MODINE TRAP

UF_6
9.08 g Tc/TON U

CLEAN-UP REACTOR

SINTERED TUBE FILTER

9.139 g Tc/TON U
(ON TUBES)

BARRIER FILTER
0.512 g Tc/TON U
(ON TUBES)

CO_2 COLD TRAPS

F_2 VENT
$<.02 \mu g/ml$ OF SAMPLE

UF_6
6.356 g Tc/TON U

Preliminary Flow Diagram For Recovery of Technetium From K-1410 Soak Tank Sol'n.

12-18-59